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HIGH ENERGY DENSITY NON-AQUEOUS BATTERY SYSTEM(U)
CENTRAL STATE UNIV WILBERFORCE OH DEPT OF CHEMISTRY
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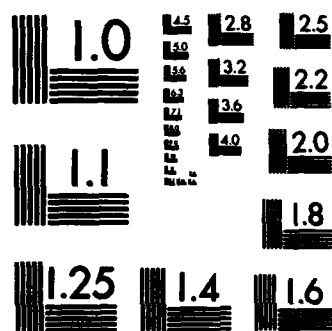
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The corrosion of the calcium anode in the calcium thionyl chloride cell has been a persistent problem which has kept this otherwise attractive couple from use. In this report are included, the corrosion studies of calcium and calcium lithium alloys in thionyl chloride electrolyte systems as a function of LiAlCl₄ concentration, time, and temperature; and investigations of cells with anodes made from calcium/calcium-lithium alloys. The results of corrosion studies indicate the following: the corrosion phenomena is very sensitive to		

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air and moisture; the corrosion occurs during storage and more rapidly at 55°C; in pure thionyl chloride the alloys appear to more resistant to corrosion than calcium metal; in electrolytes the extent of corrosion is a function of the electrolyte concentration. The anodes were made from calcium/calcium-lithium alloys in hopes of obtaining synergistic results, namely a stable anode surface film vs. pure calcium and a higher melting point than lithium anodes. The results indicate that some degree of synergism does exist but that the surface film is not sufficiently stable to protect the anode from continuous corrosion. It is concluded that the stability problem is one of a mechanical shedding of the film which occurs independent of lithium content. Also, it is felt that a change in the electrolyte salt is the most promising approach to calcium corrosion problem.

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HIGH ENERGY DENSITY NON-AQUEOUS BATTERY SYSTEM

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Objective: This research was concerned with expanding the basic understanding of non-aqueous electrolyte electrochemical cells, and in particular, the calcium thionyl chloride systems, in an attempt to reduce the self discharge rate of the cell.

Background: High energy density batteries have played an important role in various military applications as power sources (1). During the past few years various lithium battery systems have been developed to fulfill the need for long shelf life high energy density batteries. The lithium-thionyl chloride system has exhibited the capability of providing the highest energy of all the lithium systems, but it has experienced the problems of voltage delay and safety. Certain lithium properties, the low melting point (180°C), the ignition temperature (190°C in O_2), the high heat of combustion (71 kCal/eq.) present serious safety problems. In addition, burning and molten lithium may also be hazardous. A recent explosion of a large (approximately 42 kw-hr) lithium-thionyl chloride battery claimed one life and two injuries (2) (4th of August 1976, Ogden, Utah). Thus lithium batteries have not reached the general public and their use has been restricted to military applications.

The above problems have resulted in the development of an alternative system using the calcium anode (3-7). The main incentive for using calcium in place of lithium is that calcium anodes have the prospect of higher temperature operation as compared to lithium anodes. The disparity between melting points of the two metals is of special interest since the 839°C required to melt calcium would not likely be reached by any internally driven cell conditions, thus precluding the thermal runaway so often seen in the lithium thionyl chloride

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cells. Therefore, calcium thionyl chloride battery system is very attractive from the point of view of combining high energy density with a high degree of safety.

Approach: The effort involved defining the self-discharge rate, and to determine if this rate can be significantly altered by changes in the electrolyte concentration. The experiments involved use of various concentrations of the electrolyte, the preparation of alloy electrodes, determination of the optimum electrolyte concentration from conductivity and corrosion studies, and to fabricate cells based upon the results of above experiments. The corrosion rates of calcium/calcium-lithium alloys have been studied as a function of electrolyte concentration, time, and temperature, using various techniques such as electron microscope. The cells made with anodes made from calcium/calcium-lithium alloys have been investigated in terms of open circuit potentials, voltage-stability, passivation characteristics, and limiting discharge rates.

ACCOMPLISHMENTS

The studies on corrosion of Calcium/calcium-lithium alloys in thionyl chloride, in different concentrations of LiAlCl_4 in thionyl chloride, both as a function of time and temperature were reported at the 162nd meeting of The Electrochemical Society (8). The results of the above study are summarized as follows:

- o The corrosion of calcium and Calcium-lithium alloys is a significant problem.
- o The corrosion phenomena is very sensitive to air and moisture.
- o The corrosion occurs during storage and more rapidly at 55°C .
- o In pure thionyl chloride the alloys appear to be more resistant to corrosion than calcium metal.
- o 2.4% and 5.0% alloys seem to be more resistant to corrosion than 8.9% alloy.

In electrolytes the extent of corrosion is a function of the increasing concentration of the electrolyte and the following comments apply:

- o 1.2 M electrolyte seems to be suitable for batteries.
- o Calcium metal seems to be more resistant to corrosion than the alloys of calcium-lithium.
- o The film formed on the surface appears to be mechanically unstable since it periodically becomes loose with time and comes off.

The specific conductivity data (8) for pure thionyl chloride and electrolyte solutions (0.6 M, 1.2 M, and 1.8 M LiAlCl_4 in thionyl chloride) indicates that specific conductivity of the electrolyte is about three orders higher than that of pure thionyl chloride. The conductivities of the electrolyte solutions in the range of 0.6 M to 1.8 M do not vary significantly.

Based on the corrosion studies and conductivity data, open-circuit potentials (OCV) have been measured for calcium and calcium-lithium alloy anodes with carbon cathode in different concentrations of electrolyte, LiAlCl_4 in thionyl chloride. In addition, the performance characteristics, such as: open circuit potential stability, cell-voltage under load, and stability of the corrosion film in the presence of the separator material have also been studied. The results of this study have been composed in the form of a manuscript (9) that has been submitted for presentation at the 18th Intersociety Energy Conversion Engineering Conference (IECEC) to be held in Orlando Florida in August, 1983. The manuscript will also be published in the proceedings of the meeting. The results are summarized in the following paragraph.

The anodes were made from calcium/calcium-lithium alloys in the hopes of obtaining synergistic results, namely a stable anode surface versus pure calcium

and a higher melting point than lithium anodes. The results indicate that some degree of synergism does exist but that the surface film is not sufficiently stable to protect the anode from continuous corrosion. At this point it is concluded that the stability problem is one of a mechanical shedding of the film which occurs independent of lithium content in the alloy. Also, it is felt that a change in the electrolyte salt is the most promising approach to calcium corrosion problem.

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